

PATENT ABSTRACTS OF JAPAN

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(54) STAINPROOF METHOD AND STAINPROOF BASE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a stainproof method by which an outstanding performance such as resistance to wear and washing or water/oil repellency can be imparted to paper or a fibrous material and a stainproof base material.

SOLUTION: This stainproof method is performed in two steps: the first step is to form a film by applying an anionic fluorores in an emulsion composed of a monopolymer of an ethylene unsaturated monomer (A) containing the alkyl fluoride group and/or a copolymer of the ethylene unsaturated monomer (A) containing the alkyl fluoride group and an ethylene unsaturated monomer (B) containing no alkyl fluoride group, and/or a polycondensation adduct of an alcohol (C) containing the alkyl fluoride group, as essential components, or both anionic fluorores in emulsion and aqueous dispersion resin, to a base material, and the second step is to apply the cationic fluorores in emulsion to the base material and thereby, form a stainproof film.

former (B), see page 6-7, 8

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CLAIMS

[claim(s)]

[claim 1] To a substrate, as the 1st-step processing A homopolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), and/or, a copolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), and fluorinated alkyl group a non-containing ethylenic unsaturated monomer (B). And/or, a soil-resistant-finish method making an anionic form fluororesin emulsion which uses a polycondensation adduct of fluorinated alkyl group content alcohol (C) as an essential ingredient adhere to a substrate, making a coat form and making a cation form fluororesin emulsion adhere as the 2nd-step processing further.

[claim 2] A soil-resistant-finish method according to claim 1 of using together an anionic form fluororesin emulsion and aqueously distributed resin, making it adhering to a substrate in the 1st-step processing, and making a coat forming.

[claim 3] A soil-resistant-finish method according to claim 1 or 2 that coating weight to substrate weight of an

anionic form fluororesin emulsion in the 1st-step processing is 1 to 30 % of the weight, and coating weight to

substrate weight of a cation form fluororesin emulsion in the 2nd-step processing is 1 to 30 % of the weight.

[claim 4] The total amount of fluoride in a processing substrate measured by the alizarin complexone method is

0.05 to 2.0 % of the weight to substrate weight. And a soil-resistant-finish method according to any one of claims

1 to 3 that the amount of fluorine atoms which is carrying out orientation to the surface analyzed by X linear-light

electronic-spectroscopic-analysis method is 0.01 - 1atm%.

[claim 5] A soil-resistant-finish method according to any one of claims 1 to 4 that substrates are one sort chosen

from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, and knitting, or two sorts or

more of complexes.

[claim 6] A soil-resistant-finish method according to any one of claims 1 to 5 that a processing method is a method

which combined one sort chosen from the impregnating method, a spray method, and a coating method, or two

sorts or more.

[claim 7] A substrate which substrates are one sort chosen from paper, wallpaper, a nonwoven fabric, artificial

leather, synthetic leather, textiles, and knitting, or two sorts or more of complexes, and is characterized by giving

a soil-resistant-finish method according to any one of claims 1 to 6.

[translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the substrate which gave the soil-resistant-finish method which can give the outstanding performances, such as abrasion resistance, washing resistance, and water and oil repellency, and the processing method to paper or fibn material. The abrasion resistance which was superior to the processing method by the conventional fluoro-resin to paper or fibn material in detail, it is related with the soil-resistant-finish method which can give washing resistance, water and oil repellency, etc., and is related with the substrate chosen from one sort chosen from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, knitting, etc. which gave this processing method, or two sorts or more of complexes. This invention is available for wide range uses, such as garments, general merchandise, a building material, an interior raw material, a vehicle interior material, and wrapping.

[0002]

[Description of the Prior Art] As the soil-resistant-finish method of providing endurance, conventionally, for example, predrying is performed in the state where make a drainage system fluoro-resin adhere to the 1st step in JP,3-234870-A, and the water-and-oil-repelling effect is not made to reveal, and two steps of processing methods to which the fluoro-resin of an organic solvent system is made to adhere in the 2nd step are proposed. Even if this proposal uses the fluoro-resin which has water and oil repellency with pretreatment by using the 2nd step of the fluoro-resin of the high organic solvent system of penetrating power, it permeates enough, and it fills up with a fluoro-resin uniformly to a substrate, and the surface is made to reveal antifoiling property because a fluorine atom carries out orientation regularly. However, since the above-mentioned soil-resistant-finish method is using impact reduction in recent years (especially measure against VOC). The actual condition is that it is not adapted for the situation where organic solvent effluent control becomes strong. Since the organic solvent was used, and the problem of a worker's safety and hygiene and accident prevention top exposure-proof type equipment were needed, there was also a problem in respect of facility cost.

[0003]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to provide the substrate which gave the soil-resistant-finish method which can give the outstanding performances, such as abrasion resistance, washing resistance, and water and oil repellency, and this soil-resistant-finish method to paper, fibn material and artificial leather, and synthetic leather.

[0004]

[The arts means to solve] This invention persons receive paper, fibn material and artificial leather, and synthetic

leather with the specific processing method shown below, as a result of repeating examination wholeheartedly that an aforementioned problem should be solved, it finds out that the substrate which gave the soft-resistant-finishing method which can give the outstanding performances, such as abrasion resistance, washing resistance, and water and oil repellency, and this soft-resistant-finishing method can be provided, and came to complete this invention.

[0005]This invention as the 1st-step processing to a substrate Namely, the homopolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), And/or, the copolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), and fluorinated alkyl group a non-containing ethylenic unsaturated monomer alkyl group content alcohol (C) as an essential ingredient adhere to a substrate, and a coat is made to form. The soft-resistant-finishing method making a cation form fluororesin emulsion adhere as the 2nd-step processing is provided. [0006]This invention provides the substrate chosen from one sort chosen from the paper, the wallpaper, the nonwoven fabric, artificial leather, the synthetic leather, textiles, and knitting giving the aforementioned soft-resistant-finishing method, or two sorts or more of complexes.

[0007]

[Embodiment of the invention]Subsequently, in carrying out this invention, a required matter is described below concretely.

[0008]Although the substrate as used in the field of this invention can say one sort chosen from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, knitted fabric, etc., or two sorts or more of complexes and they can be arbitrarily used for it [for the purpose of these], it is not limited to these. The paper, synthetic paper which laminated synthetic resins, such as polyethylene and polypropylene, as a substrate used by these invention, for example, Textiles and knitting which consist of synthetic fibers and these improvement textiles, such as polyester and a polyacrylic; Wool, Textiles and knitting which consist of these mixed use textiles, such as textiles, semi-synthetic fibers, such as knitting; acetate and rayon, etc. which consist of natural fibers, such as silk, cotton, and hemp, **, such as fibrous sheet-like things, such as a nonwoven fabric, are mentioned, a these fibrous sheet-like thing — organic solvent system resin or drainage resin — preferably, although, **** processing, or artificial leather and synthetic leather that coating

polyurethane resin, it is not limited at all by said illustration.

[0009]Although there is no end clearly about why the antifouling property outstanding by dividing into two steps the fluororesin in which ionically differs, and processing it is revealed in this invention. To a substrate the blend liquid which used together anionic form fluororesin emulsion independence and/or an anionic form fluororesin emulsion, and aqueously distributed resin as the 1st step being impregnated, a spray, or by applying, A resinous principle adheres to a substrate firmly and gives the primary water and oil repellency and primary antifouling property to the whole substrate first. Subsequently, the fluorine concentration of a base material surface rises a cation form fluororesin emulsion being impregnated, a spray, or by applying to a substrate as the 2nd step. Thus, the obtained antifouling coat becomes possible [having water and oil repellency advanced as a result and

antifouling property]

[0010]About the mechanism of this antifouling property grant, it guesses from the viewpoint of the ionicity of a fluororesin emulsion, it is thought that the anionic form fluororesin solid content impregnated or applied to the whole substrate in the 1st step is in the state where it has not adhered to a partial substrate in [although it is the whole substrate] micro. When the cation form fluororesin which is opposite electrification in ion is impregnated or applied there in the 2nd step, it will stick to the portion to which the anion resin processed in the 1st step has not adhered, i.e., the substrate portion of non-electrification, selectively. Therefore, when the 2nd-step processing is completed, it will be in the state where the fluoro-resin adhered to the whole substrate uniformly, and it will be

thought that the coat which reveals the characteristics, such as firm endurance, antifoaming property, and water and oil repellency, is formed.

[0011] Details are explained below about the anionic form fluororesin emulsion used by this invention, and a cation form fluororesin emulsion.

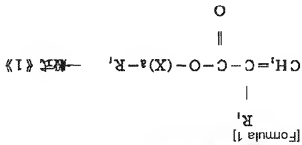
[0012] If it is a compound which has an ethylene nature unsaturation group and a fluorinated alkyl group in a

molecule as a fluorinated alkyl group content ethylenic unsaturated monomer (A) used by this invention, there will be no restriction in particular. As a fluorinated alkyl group content ethylenic unsaturated monomer (A) used by this invention, The thing containing an acrylyc ester group and its relative group is suitable from points, such as polymerization reaction nature, compatibility over other presentations in the blend liquid for processing treatment,

and an ease of acquisition, and the fluorination (meta) acrylate specifically expressed with a following general formula <1> is mentioned.

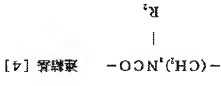
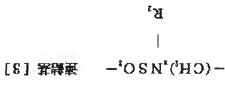
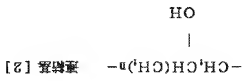
[0013] In this invention, with the blend liquid for processing treatment. All the compounds which result in the

organic solvent used for the aquosity distributed resin used at the time of the 1st step and 2nd-step impregnating processing, spray processing, or spreading processing (coating processing) and it are meant. Methacrylate, acrylate, fluoro acrylate, and chlorination acrylate shall be named acrylate (meta) generically, namely [0014]

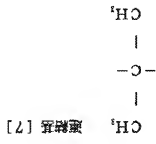
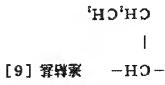
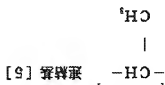


[0015] R_1 among a general formula <1> The perfluoroalkyl group of the carbon numbers 1-20, Or the thing to which it is a partial fluorination alkyl group, and the oxygen atom intervened into straight chain shape, branched state, or a main chain, To for example, everything but $-(CH_2)_n$ - which $-(OCF_2CF_2)_z$ CF_3 etc. may be sufficient, R_1 is H , CH_3 , Cl , or F , and X is a divalent connecting group, for example, is a connecting group [1]

[0016]
[Formula 2]



[0017](However, n in connecting group [1] - [4] is an integer of 1-10, and R₂ is an alkyl group of H or the carbon numbers 1-6.)
[0018]Further, [0019]
[Formula 3]



[0020]or[0021]
[Formula 4]

CF₃ 連結基 [8]

—C—

|

H

CF₃ 連結基 [9]

|

—C—

|

CF₃

CF₃ 連結基 [10]

|

—C—

|

CH₃

[0022]Being by **, a is 0 or 1. The compound expressed with], and the compound which has two or more perfluoroalkyl groups in the molecule like a general formula <<2>> [m is an integer of 1-14 among a general formula <<2>>, it is].

[0023]

[Formula 5]

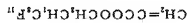
CH₂=COOCH₂CH₂C_nF_{2n+1} 一般式《2》

|

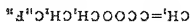
CH₂CH₂C_nF_{2n+1}

[0024]The thing like the following is mentioned as an example of the fluorinated alkyl group content (meta) acrylate used by this invention. For example, [0025]

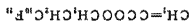
[Formula 6]

化合物 1 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_6\text{F}_{11}$ 化合物 2 : CH_2 

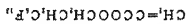
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化合物 3 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_{11}\text{F}_{22}$ 化合物 4 : CH_2 

|

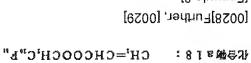
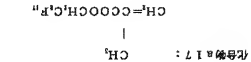
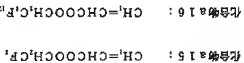
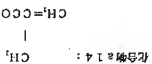
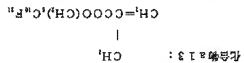
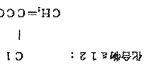
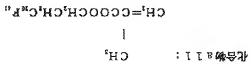
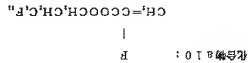
化合物 5 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_{18}\text{F}_{38}$ 化合物 6 : CH_2 

|

化合物 7 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_6\text{F}_{11}$ 化合物 8 : CH_2 化合物 9 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_6\text{F}_{11}$

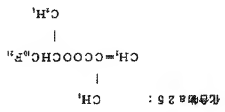
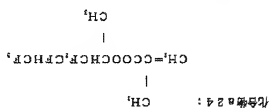
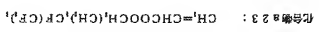
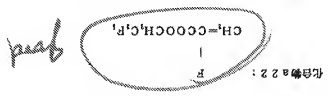
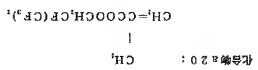
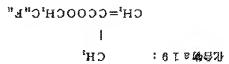
[0026]Further, [0027]

[Formula 7]



[0028] Further, [0029]

[Formula 8]

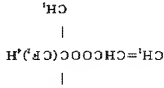
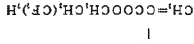
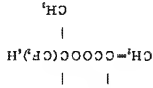
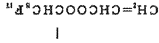


[0030]
[Formula 9]

化合物 26: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{CF}(\text{CF}_3)\text{H}$ 化合物 27: CH_3  $\text{CH}_3=\text{COOCH}_2(\text{CF}_3)\text{H}$ 化合物 28: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{H}$ 化合物 29: $\text{CH}_3=\text{CHCOOCH}_2\text{CF}_3$ 化合物 30: CH_3  $\text{CH}_3=\text{COO}(\text{CF}_3)\text{H}$ 化合物 31: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{H}$ 化合物 32: CH_3  $\text{CH}_3=\text{COOCH}_2(\text{CF}_3)\text{H}$ 化合物 33: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{H}$ 化合物 34: CH_3  $\text{CH}_3=\text{COOCH}_2(\text{CF}_3)\text{H}$ 化合物 35: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{H}$ 化合物 36: $\text{CH}_3=\text{CHCOOCH}_2(\text{CF}_3)\text{H}$

[0031]

[Formula 10]

化合物 3 7 : $\text{CH}_2=\text{CHCOOCH}_2(\text{CF}_2)_{14}\text{H}$ 化合物 3 8 : $\text{CH}_2=\text{CHCOOCH}_2(\text{CF}_2)_{16}\text{H}$ 化合物 3 9 : CH_3 化合物 4 0 : $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2(\text{CF}_2)_{14}\text{H}$ 化合物 4 1 : CH_3 化合物 4 2 : CH_3 化合物 4 3 : CF_3 化合物 4 4 : $\text{CH}_2=\text{CHCOOCH}_2\text{CF}_3$

[0032]

[Formula 11]

化合物 45: $\text{CH}_3=\text{CHCOOCH}_2\text{CHCH}_2\text{C}_6\text{F}_5$

|

OH

化合物 46:

 CH_3

|

 $\text{CH}_3=\text{CCOOCH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{F}_5$

|

OH

化合物 47:

 C_6H_5

|

 $\text{CH}_3=\text{CHCOOCH}_2\text{CH}_2\text{NSO}_2\text{C}_6\text{F}_5$

化合物 48:

 CH_3

|

 $\text{CH}_3=\text{CCOOCH}_2\text{CH}_2\text{NSO}_2\text{C}_6\text{F}_5$

化合物 49:

Cl

|

 $\text{CH}_3=\text{CCOO}(\text{CH}_3)\text{NSO}_2\text{C}_6\text{F}_5$

化合物 50:

 C_6H_5

|

 $\text{CH}_3=\text{CHCOOCH}_2\text{CH}_2\text{NSO}_2\text{C}_6\text{F}_5$

化合物 51:

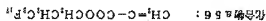
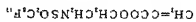
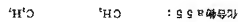
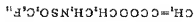
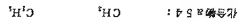
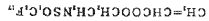
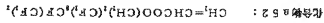
 CH_3

|

 $\text{CH}_3=\text{CHCOO}(\text{CH}_3)\text{NSO}_2\text{C}_6\text{F}_5$

[0033]

[Formula 12]



[0034] Of course, this invention is not what is limited in any way by the above-mentioned example. A fluorinated alkyl group content ethylenic unsaturated monomer (A) may use only one kind, and may use two or more kinds simultaneously.

[0035] The fluorinated alkyl group content ethylenic unsaturated monomer (A) used by this invention is introduced into intramolecular in order to adhere to the base material surface concerning this invention and to give advanced antifoaming property, water repellence, and endurance.

[0036] The carbon number of the fluorinated alkyl group in the fluorinated alkyl group content ethylenic unsaturated monomer (A) used by this invention, and/or a fluorination alkenyl group, in order to reveal the water repellence of an antifoaming coat, the range of 3-20 is preferred, and in order to reveal more advanced water repellence and to hold the stability of an emulsion, the range of 6-12 is more preferred.

[0037] The anionic form and cation form fluororesin emulsion which are used by this invention. The homopolymer produced by making one sort of the above-mentioned fluorinated alkyl group content ethylenic unsaturated monomer (A) or two sorts or more polymerize independently may be used, and copolymerization of said

unsaturated monomer (A), and the fluorinated alkyl group non-containing ethylenic unsaturated monomer (B) may be carried out. This monomer (B) can be suitably chosen according to the purpose in consideration of compatibility, polymerization reaction nature, cost, etc. to other raw materials in the blend liquid for processing treatment. In this invention, with the blend liquid for processing treatment. All the compounds which result in the various additives for revealing the performance made into the purpose besides an emulsifier, and water and an organic solvent used for the aqueously distributed resin used at the time of the 1st step and 2nd-step impregnating processing, spray processing, or spreading processing and it are meant.

[0038] A fluorinated alkyl group a non-containing ethylenic unsaturated monomer (B) used by this invention, there is no restriction in particular, and if it is a compound of publicly known public use, anything can be used. As an example of this monomer (B), for example Ethylene, propylene, Butylene, butadiene, isoprene, styrene, nucleare substitution styrene, diacetone acrylamide, Acrylonitrile, acrylamide, chloroprene, VCM/PVC, a vinylidene chloride. Fatty acid vinyl, such as vinylpyridine, N-vinyl pyrrolidone, vinylsulfonic acid, and vinyl acetate. As a derivative of carboxylic acid [of monovalence, such as alpha, beta-ethylenic unsaturated carboxylic acid, i.e.,

acrylic acid, methacrylic acid, maleic acid, butelic acid, and itaconic acid thur/or bivalence] and alpha, and beta-ethylenic unsaturated carboxylic acid. The carbon number of an alkyl group The acrylic acid alkyl ester (meta) (acrylic acid alkyl ester) shall name generally both acrylic acid and methacrylic acid alkyl ester (acrylic acid alkyl ester) of 1-18. Namely, methyl, ethyl, propyl, butyl, octyl, decyl, dodecyl, and stearyl ester (meta) ester of the carbon numbers 1-18 of acrylic acid, such as 2-ethylhexyl, decyl, dodecyl, and stearyl ester (meta), i.e., 2-hydroxy ethyl ester, hydroxy propyl ester, hydroxy butylester, etc. can be illustrated. [0039]As other monomers (B), the amino alkyl ester of the carbon numbers 1-18 of acrylic acid (meta), for example, dimethylamino ethyl ester and diethylamino ethyl ester. The carbon number of acrylic acid (meta) diethylamino propyl ester etc. The ether acid matter content alkyl ester of 3-18, for example, methoxy ethyl ester and ethoxyethyl ester and methoxy propyl ester. Methyl cull BIRUESUTERU, ethyl cull BIRUESUTERU, butyl cull BIRUESUTERU, etc., a bridged bond content monomer (for example, dicyclopentaniil oxy ethyl (meta)-acrylate), isobornyl (meta) acrylate, isobornyl (meta) acrylate, Adamantyl (meta) acrylate, dimethyl adamantyl (meta) acrylate, Dicyclopentaniil(metha)acrylate, JISHIKURC pentyl (meta) acrylate, etc., an alkyl carbon number — alkyl vinyl ether (for example, the methyl vinyl ether, propylvinyl ether, dodecylvinyl ether, etc.) of 1-18, and glycidyl ester (for example, glycidyl methacrylate, glycidyl acrylate, etc.) of acrylic acid (meta) — further, The various macro monomers of the Sartomer styrene macro monomer 4500, Tgooseel AA-6, and AA-6 grade can be illustrated. [0040]As other fluorinated alkyl group non-containing ethylenic unsaturated monomers (B) used by this invention, a silane KAPFUNGU group content monomer (gamma-methacryloxypropyl methoxysilane). Gamma-methacryloxypropyl dimethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-acryloxypropyl methyl trimethoxysilane, gamma-acryloxypropyl dimethoxysilane, the monomer (acrylic acid) which contains a polar group division anionlic group and a hydroxyl group in molecules, such as a vinyl TORIMECHIL gendate tri, run Methacrylic acid, 2-(meta) acryloxyloxyethyl succinic acid, 2-acrylamido-2-methyl propane sulfonic acid, partial sulfonation styrene, Mono-(acryloxyloxyethyl) acid phosphate, mono-(methacryloxyethyl) acid phosphate, the silicone mono-(meta) acrylate which has a poly dimethylsiloxane chain, such as 2-hydroxyethyl (meta) acrylate and 2-hydroxypropyl (meta) acrylate, the acrylate (meta) containing a polyoxyalkylene group, a vinyl

system monomer, etc. are mentioned. [0041]Of course, this invention is not what is limited in any way by the above-mentioned example. Only one kind may be used for fluorinated alkyl group the non-containing ethylenic unsaturated monomer concerning this invention (B), and two or more kinds may be simultaneously used for it.

[0042]Although the rate of obtaining as a copolymer the anionic form and cation form fluororesin emulsion which are used by this invention (A), and said monomer (B) changes with the blend liquid presentation for processing treatment, the performance levels of the antifouling coat made into the purpose, coating methods, etc., it is the range of (A)/(B) = 5 - 95/95 - 5 weight ratio preferably, is the range of (A)/(B) = 30 - 80/70 - 20 weight ratio more preferably, and is the range of (A)/(B) = 40 - 70/60 - 30 weight ratio especially preferably.

[0043]It is preferred any of the melting point of the polymer of an anionic form and a cation form fluororesin emulsion, a glass transition point or flow beginning temperature, and softening temperature which are used by this invention they are, and it is not less than 20 °, and is the range of 50-160 °, more preferably. A homopolymer and a copolymer are also included in the field of this invention. [0044]The ranges of the weight average molecular weight of the polymer of the anionic form and cation form fluororesin emulsion which are used by this invention are 700-100,000 preferably, and the ranges of it are 3,000-30,000 more preferably. If it is this range, the outstanding endurance, antifouling property, and the adhesion to a substrate can be acquired. [0045]Although there is no restriction in the manufacturing method of the homopolymer concerning this invention, or a copolymer in any way and it can manufacture based on polymerization mechanisms, such as a publicly

known method, i.e., a radical polymerization method, a cationic polymerization method, and an anionic polymerization method, by solution polymerization method, mass polymerization method, an emulsion polymerization method, etc., especially a radical polymerization method is simple and industrially preferred. [0046] In this case — as a polymerization initiator — this industry — a publicly known thing can be used, for example, azo compounds, such as benzoyl peroxide and hypoxodation diacyl, azobisisobutyronitrile, and phenylazo triphenylmethane, metal chelate compound, etc., are mentioned. [0047] Chain transfer agents, such as lauryl mercaptan, 2-mercaptoethanol, ethyldithioglycolic acid, and octylthioglycolic acid, and also coupling group content thiol compounds, such as gamma-mercaptopropyltrimethoxysilane, can be used if needed.

[0048] Also by the polymerization which makes an energy source photopolymerization or the radiation under existence of a photosensitizer and a photoinitiator, and heat, it can be random in the fluorine system concerning this invention, or a block copolymer can be obtained.

[0049] Although either under existence of a solvent or nonexistence can carry out a polymerization reaction, especially limitation is not carried out, as a solvent in which the direction in under solvent existence is preferred, and uses, for example, ethanol, isopropyl alcohol, n-butanol, iso-butanol, Alcohols, such as tert-butanol, Acetone, methyl ethyl ketone, Ketone, such as methyl isobutyl ketone and methyl amyl ketone, Ester, Ester species, such as ethyl acetate, butyl lactate, and butyl lactate; 2-hydroxypropionic acid methyl, 2-methoxypropionic acid ethyl, 2-hydroxypropionic acid propyl, 2-hydroxypropionic acid butyl, 2-methoxy methyl propionate, 2-methoxy ethyl propionate, 2-methoxy propionic acid propyl, Monocarboxylic acid ester species, such as 2-methoxy butyl propionate; Dimethylformamide, Polar solvents, such as dimethyl sulfoxide and N-methyl pyrrolidone; Methyl cellosolve, Ethyl cellosolve, butyl cellosolve, butylcarbitol, and ethylcellosolve acetate; Propylene glycol, propylene glycol monomethyl ether, propylene-glycol monomethyl ether acetate, Propylene glycol, ester species of those, such as propylene glycol monomethyl ether acetate and propylene glycol monobutyl ether acetate; 1,1,1-trichloroethane, halogen system solvent, such as chloroform, 1,1,1-tetrahydrofuran; — ether, such as dioxane, — aromatic hydrocarbon, such as benzene, toluene and xylene, — all of fluorination inert liquids, such as perfluorooctane and perfluorooctyl-n-butylamine, can be used further. Of course, this invention is not what is limited in any way by the above-mentioned example.

[0050] Initiator concentration and chain transfer agent concentration can usually adjust the weight average molecular weight of the polymer of the anionic form and cation form fluorosin emulsion which are used by this invention in the desirable range.

[0051] As an anionic form fluorosin emulsion used by this invention, although the homopolymer of the above-mentioned fluorinated alkyl group content ethylenic unsaturated monomer (A) and/or the copolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), and fluorinated alkyl group a non-containing ethylenic unsaturated monomer (B) can be used as above-mentioned, in addition, the polycondensation adduct of fluorinated alkyl group content alcohol (C) can also be used.

[0052] With the polycondensation adduct of the fluorinated alkyl group content alcohol (C) used by this invention, Monovalence or polyhydric alcohol in which the monovalence or polyhydric alcohol in which a carbon number contains the fluorinated alkyl group and/or fluorination alkyl group of 3-20, and a carbon number have a hydrocarbon system skeleton of 3-30, And the weight average molecular weight obtained by a polycondensation with the carboxylic acid (poly) in which a carbon number does not contain or contain the fluorinated alkyl group which are 4-20 is preferred, and they are 1000 or more ester compounds (poly), [0053] Monovalence or polyhydric alcohol in which the monovalence or polyhydric alcohol in which a carbon number contains the fluorinated alkyl group and/or fluorination alkyl group of 3-20, and a carbon number have a hydrocarbon system skeleton of 3-30, and the weight average molecular weight obtained by the polycondensation of the organic (poly) isocyanates 30, and the weight average molecular weight obtained by the polycondensation of the epoxy group content

monomer containing the fluorinated alkyl group and/or fluorination alkyl group of the carbon numbers 3-20, and the poly RfREN oxide which does not contain a fluorinated alkyl group. Or the weight average molecular weight obtained by a polycondensation with the epoxy compound of publicly known public use, such as epichlorohydrin, says 3000 or more polycondensation addition.

[0055] fluorinated alkyl group content (poly) carboxylic acid can use alcohol and (poly) carboxylic acid containing the fluorinated alkyl group of publicly known public use. As an example of the raw material which constitutes this polycondensation adduct, the compound shown below is

mentioned, for example.

[0056]

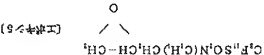
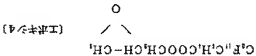
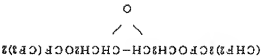
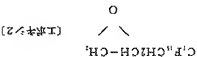
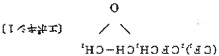
compound C1: $C_6F_{13}CH_2CH_2OH$ compound C2: $C_7F_{15}CH_2CH_2OH$ compound C3: $C_7F_{15}CH_2OH$ compound C4: $C_6F_{17}CH_2CH_2OH$ compound C5: $C_6F_{13}SO_2N(CH_3)CH_2CH_2OH$ compound C6: $C_6F_{13}SO_2N(C_3H_7)CH_2CH_2OH$ compound C7: $C_6F_{17}SO_2N(C_2H_5)CH_2CH_2OH$ compound C8: $C_6F_{17}O(C_6H_4)CH_2CH_2OH$ compound C9: $C_6F_{15}CON(C_2H_5)CH_2CH_2OH$ compound C10: $C_{10}F_{19}N(C_2H_5)CH_2CH_2OH$ compound C11: $C_7F_{15}COOH$ compound C12: $C_9F_{17}O(C_6H_4)COOH$ compound C13: $C_8F_{17}SO_2N(C_3H_7)CH_2COOH$ compound C14: $C_8F_{17}CH_2CH_2COOH$ HCOOH [0057]As an example of the above-mentioned carboxylic acid, for example Succinic acid, adipic acid, azelaic acid, sebacic acid, Subah Ching acid, trimellitic acid, dodecane dicarboxylic acid, A maleic anhydride, fumaric acid, 1,4-cyclohexane dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, Phthalic acid, 1,4-naphthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, naphthalic acid, biphenyl dicarboxylic acid, The anhydride or ester plasticity derivative of 1,2-bis(phenoxyl)ethane-p,p'-dicarboxylic acid and these dicarboxylic acid, the ester plasticity derivative of para-hydroxybenzoic acid, p-(2-hydroxyethoxy) benzoic acid, and these hydroxycarboxylic acid, etc. mention, and it is ****.

[0058]As the monovalence of a hydrocarbon system, or an example of polyhydric alcohol, for example, ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, a polypropylene glycol, Glycerin, ethylene glycol monomethyl ether, 2-ethylhexanol, Stearyl alcohol, diethylene glycol, triethylene glycol, Tetraethylene glycol, a polyethylene glycol (molecular weights 300-6,000), Dipropylene glycol, tripropylene glycol, screw hydroxyethoxybenzene, 1,4-cyclohexanediol, 1,4-cyclohexane dimethanol, bisphenol A, hydrogenation bisphenol A, hydroquinone, those alkylene oxide adducts, etc. are mentioned.

[0059]As an example of organic (poly) isocyanates, For example, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, diphenylmethane diisocyanate, and 4 and 2,4'-diphenylmethane diisocyanate, 2,2'-diphenylmethane diisocyanate, the 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, 1,5-tetrahydronaphthalene diisocyanate, tetramethylene diisocyanate, 1,3-1,6-hexamethylenediisocyanate, dodeca methylene diisocyanate, Trimethyl hexamethylene diisocyanate, 1,3-cyclohexylene diisocyanate, 1,4'-cyclohexylenediisocyanate, xylene diisocyanate, tetramethyl xylene diisocyanate, hydrogenation xylene diisocyanate, lysine diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, the 3,3'-dimethyl-4,4'-dicyclohexylmethane diisocyanate, etc. are mentioned. [0060]The compounds following, for example as an epoxy group content monomer containing the fluorinated alkyl group and/or fluorination alkyl group of the carbon numbers 3-20 used by this invention, [Epoxy 5] ** is mentioned. Of course, this invention is not what is limited in any way by the following example.

[0061]

[Formula 13]



[0062] The polycondensation adduct of the fluorinated alkyl group content alcohol (C) used by this invention An ester compound (poly), O, or urethane compound (poly) and an epoxy compound independent may be sufficient, and it does not matter even if it is an ester compound (poly), a urethane compound (poly), and two or more sorts of mixtures of the epoxy compounds.

[0063] The fluororesin emulsion used by this invention is obtained by emulsifying the above-mentioned compound with an emulsifier. Although the emulsifier used in that case can use the compound of publicly known public use, since the fluororesin emulsions used for the 1st step and the 2nd step are an anionic form and a cation form, respectively, it must be used in consideration of the ionicity by this invention. That is, a cation form must be used for the fluororesin emulsion for antifoaming coat formation of the 2nd step at the fluororesin emulsion for antifoaming coat formation of the 1st step using an anionic form. However, it can be used also when emulsifying which fluororesin emulsion about a nonionic emulsifier.

[0064] As an example of the emulsifier used by this invention, for example Polyoxyethylene nonylphenyl ether, Polyoxyethylene lauryl ether, polyoxyethylene styrene-ized phenyl ether, The Nonion system emulsifiers, such as polyoxyethylene sorbitol tetra oleate, Fatty acid salt, such as sodium oleate, Alkyl-sulfonic-acid ester salt, alkylbenzene sulfonate, alkyl sulfosuccinate, Naphthalene sulfonate, alkane sulfonate sodium salt, Anionic system emulsifiers, such as an alkyl diphenyl ether specific sulfonate salt, Polyoxyethylene alkyl sulfate, Cation system emulsifiers, such as the Nonion anionic system emulsifiers, such as polyoxyethylene alkylphenyl sulfate, and alkyl trimethylammonium salt, the special emulsifier of a fluorene system and a silicone series, etc. are mentioned. [0065] Since desired water and oil repellency is revealed and it has the outstanding endurance and antifoaming property, the anionic form fluororesin emulsion used by this invention and a cation form fluororesin emulsion contain a fluorene atom in 10 to 60% of the weight of the range more preferably 5% of the weight or more during a presentation.

[0066] It is preferred to use together an anionic form fluororesin emulsion and aqueously distributed resin, to make it adhere to a substrate in the 1st-step processing in this invention, and to make a coat form. In the antifoaming coat

formation process of the 1st step, since the binder role of an anionic form fluororesin emulsion and a substrate is played and also the improvement in binding nature with a substrate and waterproofness, and abrasion resistance are provided. It becomes an effective means to use aqueously distributed resin together.

[0067] As aqueously distributed resin used by this invention, although each resin of publicly known public use can use it. For example, polyurethane resin, polyester resin, polyvinyl chloride resin, An epoxy resin, phenol resin, melamine resin, ethylene/vinyl chloride copolymer, Polyacrylic ester resin, styrene/butadiene copolymer, styrene / butadiene / acrylic ester copolymer, An acrylonitrile butadiene copolymer, an acrylic acid ester butadiene / styrene copolymer, An acrylonitrile butadiene copolymer, vinyl acetate resin, vinyl acetate/acrylic ester copolymer, and styrene/acrylic ester copolymer, a macromolecular latex emulsion, etc. are mentioned.

[0068] The ratio of both in the case of an anionic form fluororesin emulsion and a binder, i.e., aqueously distributed resin, being mixed, and using in the 1st-step processing concerning this invention, in a solid content weight ratio, it is the range of 4 / 100 - 30 / 100 preferable, and is the range of 7 / 100 - 15 / 100 more preferably. If an anionic form fluororesin emulsion and aqueously distributed resin are mixed and used by the solid content weight ratio of this range, the emulsifying and antifouling property and endurance can be revealed.

[0069] In the soil-resistant-finish method of this invention, the coating weight to the substrate weight of the anionic form fluororesin emulsion in the 1st-step processing is 1 to 30 % of the weight preferably, and the coating weight to the substrate weight of the cation form fluororesin emulsion in the 2nd-step processing is 1 to 30 % of the weight preferably.

[0070] The treatment bath concentration of the 1st step concerning this invention and the 2nd step must be determined in consideration of the balance of the cost generated by military requirement levels, such as endurance and antifouling property, and processing. In order to maintain performance and to reveal a cost merit, the treatment bath concentration of any of the 1st step and the 2nd step is converted into resin solid content, its 0.05 to 10.0 % of the weight is preferred, and its 0.2 to 5 % of the weight is more preferred.

[0071] The concentration (it measures by the alizarin complexone method) of the fluorine element of the whole last processing substrate which gave the soil-resistant-finish method of this invention is 0.05 to 2.0 % of the weight preferably to substrate weight, and is 0.10 to 1.1 % of the weight of a range more preferably. The fluorine atom concentration (it measures by X linear-light electronic-spectroscopic-analysis method) of the surface is 0.01 - 1.0 % preferably, and is 0.05 - 0.50 % of a range more preferably.

[0072] The fluorine element concentration of the whole processing substrate in this invention, Dottie Al Husson (made by , Inc. Dojin Chemical Laboratory) who is a colorimetry reagent of a fluorine atom is used, and it is the quantified by the analytical method (it carries out the colorimetry of the fluorine acid which carried out decomposition generation), and the fluorine atom concentration of the surface. The fluorine atom concentration (atm) obtained by XPS (X-Ray Photoelectron Spectroscopy, X-ray photoelectron spectroscopy) analysis using the AXIS-HS type by KRATOS is meant.

[0073] In this invention, the publicly known method usually used can be used as a method of making a fluororesin method, the coating dpp'ing method, etc. can be chosen suitably, and can be used, or may combine and use. After making the liquid which contains a fluororesin emulsion by the above methods adhere, heat adherence by desiccation and curing can be performed.

[0074] Although the drying condition after concrete resin adhesion does not carry out limitation in particular, after making the aqueously distributed resin which plays a role of the anionic form fluororesin emulsion of the 1st step, and a binder adhere to a substrate. Usually, it is preferably required, 80 ° - 200 ° of time, i.e., drying time until the processed resin is not eluted to the cation form fluororesin emulsion of the 2nd step, until a processing substrate gets dry at 100 ° - 140 ° more preferably. Subsequently, the cation form fluororesin emulsion of the

2nd step is made to adhere, and 80 ** - 200 ** of the desiccation and curing for 30 seconds - 10 minutes are usually more preferably suitable for desiccation and the conditions which carry out curing at 120 ** - 180 ** preferably.

[0075]As a substrate which gave the soil-resistant-finish method of this invention, one sort chosen from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, and knitting or two sorts or more of complexes etc. are mentioned, for example.

[0076]As a use of the processing substrate which gave the soil-resistant-finish method of this invention, it can apply to various fields, such as garments, a building merchandise, an interior raw material, a vehicle interior material, and wrapping, for example.

[0077]As mentioned above, the mode of this invention as the 1st-step processing to a substrate The homopolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), And/or, the copolymer of a fluorinated alkyl group content ethylenic unsaturated monomer (A), and fluorinated alkyl group a non-containing ethylenic unsaturated monomer (B), And/or, make the anionic form fluororesin emulsion which uses the polycondensation adduct of fluorinated alkyl group content alcohol (C) as an essential ingredient adhere to a substrate, and a coat is made to form. The soil-resistant-finish method making a cation form fluororesin emulsion adhere as the 2nd-step processing is started.

[0078]As one of the modes of other of this invention, the above-mentioned soil-resistant-finish method of using together an anionic form fluororesin emulsion and aqueously distributed resin, making it adhering to a substrate, and making a coat forming is started in the 1st-step processing.

[0079]As one of the modes of other of this invention, the coating weight to the substrate weight of the anionic form fluororesin emulsion in the 1st-step processing is 1 to 30 % of the weight. And the coating weight to the substrate weight of the cation form fluororesin emulsion in the 2nd-step processing is applied to each of above-mentioned

[0080]As one of the modes of other of this invention, the total amount of fluoride in the processing substrate measured by the alizarin complexone method is 0.05 to 2.0 % of the weight to substrate weight. And the amount of fluorine atoms which is carrying out orientation to the surface measured by X linear-light electronic-spectroscopic-analysis method is applied to each of above-mentioned soil-resistant-finish methods which are 0.01 - 1atm %.

[0081]As one of the modes of other of this invention, a substrate is applied to each of above-mentioned soil-resistant-finish methods which are one sort chosen from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, and knitting, or two sorts or more of complexes.

[0082]As one of the modes of other of this invention, a processing method starts each of above-mentioned soil-resistant-finish methods which are methods combined one sort chosen from the impregnating method, a spray method, and a coating method, or two sorts or more.

[0083]As one of the modes of other of this invention, it is one sort chosen from paper, wallpaper, a nonwoven fabric, artificial leather, synthetic leather, textiles, and knitting, or two sorts or more of complexes, and the substrate which gave each of above-mentioned soil-resistant-finish methods is started.

[0084]Hereafter, an example and a comparative example explain this invention much more concretely. Unless a notice has % especially in below, it is a weight reference altogether. The various characteristics of the sample were measured by the following methods. This invention is not limited only to these examples.

[0085]Practice of A C test As shown in Table 1, water was mixed with isopropyl alcohol at the rate of a constant ratio as a standard testing liquid, and a "series" was given as a name which expresses water-repellent strength gradually to each solution. The water repellence of the processing substrate was quantitatively evaluated with the water-repellent highest-class number uses a dropper for a processing base material surface, respectively, and

trickles this standard testing liquid in fixed quantity, and permeance is not accepted to be at all by after-progress

wiping for 5 minutes.

[0086]PRACTICE OF OR (oil resistance test) As shown in Table 2, As a standard examination solvent which gave

oil-repellent "series", various organic solvents in which surface tension differs are dropped at a processing

substrate in fixed quantity. The oil repellency of the processing substrate was quantitatively evaluated with a

series of the highest oil repellency of the standard testing liquid to which permeance is not accepted at all by

wiping using the method (based on an AATCC-118-1981/hydrocarbon resistance test) of observing the osmosis

state of the drop after 30 second passage.

[0087]PRACTICE OF a stain test) Using the coffee and vegetable oil which held temperature at 50 °C, respectively,

and deep soy sauce, a fixed quantity of drops of each contamination liquid were dropped, it wiped off lightly

with tissue paper 5 minutes afterward, and the degree of silverfish to the precessing substrate side of each

contamination liquid was observed visually. When displaying the degree of silverfish, the following judging

standard was followed and it evaluated. The judging standard after contamination liquid wiping is as follows.

O : marks do not remain at all after wiping.

** : After wiping, although some thing stain is made, it is not conspicuous.

X : After wiping, marks remain and it is dramatically conspicuous clearly.

[0088]<Example 1> as the 1st-step processing — an anionic form fluoro-resin emulsion water and oil repellent

agent (the Daiippon Ink & Chemicals, Inc. make), Aqua Franc TE-5A and the 5-% of the weight solution of 20

of the weight of solid content were wrung using the nip roll after impregnating a filter paper (TYPE2 by Toyo Roshi

Kaisha, Ltd., basis weight 130 g/m²), and hot air drying was carried out for 5 minutes at 100 °C, this processing

treatment finishing filter paper of the 1st step — as the 2nd-step processing — a cation form fluoro-resin emulsion

water and oil repellent agent (the Daiippon Ink & Chemicals, Inc. make), After being impregnated and wringing

the DIK(R) guard F-80 and the 5-% of the weight solution of 20 % of the weight of solid content with a nip roll, hot

air drying was performed for 5 minutes at 160 °C, and the processing substrate (X1) which gave the antifoiling

coat of the endurance of this invention was obtained.

[0089]About the above-mentioned processing substrate (X1), evaluation of the water and oil repellency before

and behind friction durability test and antifoiling property was carried out. Friction durability test used the calico

cloth for the wear cloth based on JIS-L-1042 using the abrasion tester of Gakushin-type, and carried out 3000

soy sauce as an index of OR test and antifoiling property as an oil-repellent index, and carrying out a stain test.

The result was indicated to Table 3.

[0090]The fluorene concentration of the processing substrate was collectively shown in Table 3. The concentration

Husson (made by J. Inc. Dojin Chemical Laboratory) who is a colorimetry reagent of a fluorene atom is used, and it

is the alizarin complexone method (in oxygen), [bun and] Mean the fluorene element concentration (% of the

weight) quantified by the analytical method which carries out the colorimetry of the fluorene acid which carried out

(atm) obtained using the AXIS-HS type by KRAATOS by the XPS analysis method (X-ray photoelectron

spectroscopy, X-ray photoelectron spectroscopy) is meant.

[0091]<Example 2> in the 1st-step impregnating processing in Example 1, it is an anionic form fluoro-resin

water and oil repellent agent aqua franc. It adds to the 5-% of the weight solution of TE-5A. The processing

substrate (X2) which gave the antifoiling coat of the endurance of this invention like Example 1 was obtained

except using together the 30-% of the weight blend liquid of an acrylic emulsion (the Daiippon Ink & Chemicals,

Inc. make, BONKOTO AN-185, 40 % of the weight of solid content, Tg30 °C) as a binder.

[0092]<Example 3> In the 1st-step impregnating processing in Example 1, it is an anionic form fluororesin emulsion water and oil repellent agent Aqua franc. It adds to the 5-% of the weight solution of TE-5A. The processing substrate (X3) which gave the antifoiling coat of the endurance of this invention like Example 1 was obtained except using together the 30-% of the weight blend liquid of an acrylic emulsion (the Daihippon Ink & Chemicals, Inc. make, BONKOTO AB-782, 40% of solid content weight, Tg-30 °) as a binder.

[0093]<Example 4> In the 1st-step impregnating processing in Example 1, it is an anionic form fluororesin emulsion water and oil repellent agent Aqua franc. It adds to the 5-% of the weight solution of TE-5A. The processing substrate (X4) which gave the antifoiling coat of the endurance of this invention like Example 1 was obtained except using together the 30-% of the weight blend liquid of aqueous polyurethane resin (Dainippon Ink & Chemicals, Inc. make and Bon Dik 2250, 40 % of the weight of solid content) as a binder.

[0094]<Comparative example 1> In the 1st-step impregnating processing in Example 1, an anionic form fluororesin emulsion water and oil repellent agent is not used. And the processing substrate (Y1) which gave the coat like Example 1 was obtained except having used the cation form fluororesin emulsion water and oil repellent agent DIKKU guard's F-90 10% solution by the 2nd-step impregnating processing.

[0095]<Comparative example 2> In the 1st-step impregnating processing in Example 1, it is an anionic form fluororesin emulsion water and oil repellent agent Aqua franc. Concentration of TE-5A is used as solution 10%.

And the processing substrate (Y2) which gave the coat like Example 1 was obtained except not using a fluorine system water and oil repellent agent in the 2nd-step impregnating processing.

[0096]<Comparative example 3> Fluorine system water and oil repellent agent DIKKU guard who uses toluene as an organic solvent in the 2nd-step impregnating processing. Although the durable antifoiling coat was obtained like Example 1 except having diluted NH-10 in the solution 5% by white spirit further, and having used it, in spite of the organic solvent at the time of the 2nd-step impregnating processing having volatilized and having installed the local exhaust ventilation, the workplace was full of the solvent smell and it checked that it was not desirable for reasons of sanitation [work environment].

[0097]
Table 1]

表 1	イソプロピルアルコール/水の混合比率	撥水性の級数	(体積比率)
1 級	2 / 98	2 級	5 / 95
2 級	1 0 / 9 0	3 級	2 0 / 8 0
3 級	3 0 / 7 0	4 級	4 0 / 6 0
6 級	5 0 / 5 0	7 級	6 0 / 4 0
8 級	7 0 / 3 0	9 級	

[0100]

[Effect of the invention]This invention uses together anionic form fluororesin emulsion independence or this emulsion, and aqusily distributed resin as the 1st-step processing, make it adhere to a substrate, it makes a coat form, and ranks second. The substrate which gave the soil-resistant-finish method making a cation form fluororesin emulsion adhere to a substrate as the 2nd-step processing, and making a coat form, and this processing method is provided. In order that the soil-resistant-finish method of this invention not only can give the performance which was excellent in water and oil repellency, abrasion resistance, washing resistance, etc. to paper or fibn material, but may not use an organic solvent, it is also one of the features that it is the processing method which considered environment. As a use of the processing substrate which gave the soil-resistant-finish method of this invention, it can apply to various fields, such as garments, general merchandise, a building material, an interior raw material, a vehicle interior material, and wrapping, and is not limited in particular, for example.

[Translation done.]

STAINPROOF METHOD AND STAINPROOF BASE MATERIAL

Patent numbers: JP2003154307
 Publication date: 2003-05-27
 Inventors: HASHIGUCHI TSUNENORI; TANAKA KAZUYOSHI
 Applicant: DAINIPPON INK & CHEMICALS
 Classification: International: B05D5/00; B32B27/30; C08F20/24; C08K3/00; D06M15/27; D06M15/576
 Application number: JP20020199857 20020709
 Priority number(s): JP20010229477 20010730; JP20020199857 20020709

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Abstract of JP2003154307

PROBLEM TO BE SOLVED: To provide a stainproof method by which an outstanding performance such as resistance to wear and washing or water/oil repellency can be imparted to paper or a fibrous material and a stainproof base material. SOLUTION: This stainproof method is performed in two steps: the first step is to form a film by applying an anionic fluorores in an emulsion composed of a monopolymer of an ethylene unsaturated monomer (A) containing an alkyl fluoride group and/or a copolymer of the ethylene unsaturated monomer (A) containing the alkyl fluoride group and an ethylene unsaturated monomer (B) containing no alkyl fluoride group, and/or a polycondensation adduct of an alcohol (C) containing the alkyl fluoride group, as essential components, or both anionic fluorores in emulsion and aqueous dispersion resin, to a base material, and the second step is to apply the cationic fluorores in emulsion to the base material and thereby, form a stainproof film.

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識別記号	P 1
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(54) 【発明の名称】 防汚加工方法、及び該加工方法を施した基材

(57) 【要約】

【課題】 紙や繊維基材に対して、耐摩耗性、耐洗濯性、撥水性などの優れた性能を付与出来る防汚加工方法と、該加工方法を施した基材を提供する。
【解決手段】 2段階で行う加工方法であり、基材に対して、第1段階目の加工としてフッ素化アルキル基含有エチレン性不飽和単量体 (A) の単独重合体、及び/又フッ素化アルキル基含有エチレン性不飽和単量体 (A) とフッ素化アルキル基含有エチレン性不飽和単量体 (B) との共重合体、及び/又はフッ素化アルキル基含有アルコール (C) の重縮合付加体を必須成分とするフッ素型フッ素樹脂エマルジョン、又は該エマルジョンと水性分散型樹脂とを併用し、基材に付着させ成膜を形成させ、次いで、第2段階目の加工としてカチオン型フッ素樹脂エマルジョンを基材に付着させ防汚成膜を形成させる。

【請求項1】 基材に対して、第1段階目の加工として

フッ素化アルキル基含有エチレン性不飽和単体（A）

の単独重合体、及び／又はフッ素化アルキル基含有エ

チレン性不飽和単体（B）との主重合体、及び／又は

フッ素化アルキル基含有アルコロール（C）の直鎖合付

重合体を必須成分とするアミノ型フッ素樹脂エチレン

ジンを基材に付着せしめ被膜を形成せしめ、更に、第2段階目

の加工として、フッ素化エチレン性不飽和単体（A）を付着

せしめ、第2段階目の加工方法、

【請求項2】 第1段階目の加工において、アミノ型

フッ素樹脂エチレンジンを水分分散型エチレンジンを併用し、

被膜を形成せしめ、第2段階目の加工方法、

【請求項3】 第1段階目の加工におけるアミノ型フ

ッ素樹脂エチレンジンの基材重量に対する付着量が1〜

30重量％であり、且つ、第2段階目の加工における付

着量が1〜30重量％であり、且つ、X線光電子分光分析法に

て分析した表面に配向しているフッ素原子量が0.01

〜0.5重量％である請求項1〜3の何れか一項に記載の防

防加工方法、

【請求項4】 アリシリンコポリン法にて調製し

た加工基材中のフッ素量が基材重量に対して0.05

〜0.5重量％であり、且つ、X線光電子分光分析法に

て分析した表面に配向しているフッ素原子量が0.01

〜0.5重量％である請求項1〜3の何れか一項に記載の防

防加工方法、

【請求項5】 基材が、紙、塩化、不織布、人工皮革、合

成皮革、織物、及び織物をより選ばれた1種、又は2種以

上の複合体である請求項1〜4の何れか一項に記載の防

防加工方法、

【請求項6】 加工方法が、浸漬法、スプレー法、コー

ティング法より選ばれた1種、又は2種以上を組み合わ

せしめ、第2段階目の加工方法、

【請求項7】 基材が、紙、塩化、不織布、人工皮革、合

成皮革、織物、及び織物をより選ばれた1種、又は2種以

上の複合体であり、請求項1〜6の何れか一項に記載

の防加工方法を施したことを特徴とする基材、

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、紙や繊維材料に対

し、耐摩耗性、耐油性、耐水溶性、耐水蒸気性などの優れた性

能を付与する防加工方法、及び加工方法を施した基

材に関する、更に詳しくは、従来のフッ素樹脂による加

工方法よりも、紙や繊維材料に対して優れて耐摩耗性、

耐油性、耐水溶性、耐水蒸気性などの優れた性能を付与する防加工方法を施したことを特徴とする防加工方法、

する、本発明は、表面、断面、縦断、横断、建築材料、インテグ

ラート、導電材料、包封材料などの広範囲の用途に利用可

能である。

【0002】 従来、耐久性を具備する防加工方法と

しては、例えば、特開平3-234870号公報に於いて、第2

段階目の加工方法、第2段階目の加工方法、第2段階目の加工方法、

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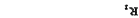
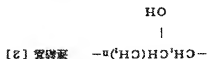
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【0017】(但し、連結基[1]～[4]中のnは1～10の整数であり、R₂はHまたは炭素数1～6のアルキル基である。)

【0018】更に、

【0019】

【化3】



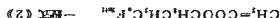
連結基 [6]



連結基 [7]



連結基 [7]



一般式《2》

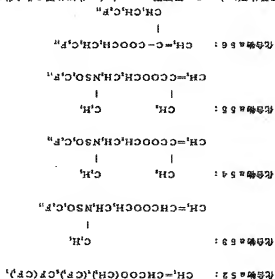
【0024】本発明で使用するフッ素化アルキル基含有

(メタ)アクリレートの特例として、以下の如き

のが挙げられる。例えば、

【0025】

【0034】尚、本発明が上記具体例によって、何等限
定されるものでないことは勿論である。また、フッ素化
アルキル基含有エチレン性不飽和重合体(A)は1種類
だけをを用いても構わないし、2種類以上を同時に用いて
も構わない。

[illegible]

(8) 003-154307 (P2003-05807)

[illegible][illegible]

$[0010]$ [illegible]

表 2 溶剤性の解放		使用した標準試験溶液名	(mN/m)
0級	溶剤性が1級に及ばないもの	—	—
1級	アセチル	3.1, 4.5	
2級	$B/A = 0.495^{\circ} B = 65/75$ 体積比	2.9, 6.0	
3級	$n = 1.54$	2.7, 3.0	
4級	$n = 1.5$ トリブレン	2.6, 3.5	
5級	$n = 1.47$	2.4, 7.0	
6級	$n = 1.45$	2.3, 5.0	
7級	$n = 1.4$ トリブレン	2.1, 4.0	
8級	$n = 1.35$	1.9, 7.5	

【参考】

可能であり、特に限定されるものではない。

フロンティアの続き

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D O 6 M 15/576

F I

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 BB912 BB92Y BB92Z CA02
 CA31 CA34 CA36 CA37 CA404
 DB16 DB18 DB20 DB36 DB43
 DB48 DB53 DB02 DB03 DC13
 DC36 DC38 EA06 EA13 EB12
 EB13 EB14 EB15 EB16 EB19
 EB20 EB22 EB32 EB33 EB35
 EB38
 4F100 AKT1B AL05B AT00A BA02
 BA10A BA10B DG10A DG12A
 EH862 EJ82Z GB08 GB15
 GB33 J106 J401B Y100
 4J100 AM02Q AM03Q AM04Q AB02Q
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 4L033 AM01 AM04 AB04 AB09 ACT5
 BA21 CA22 CA70